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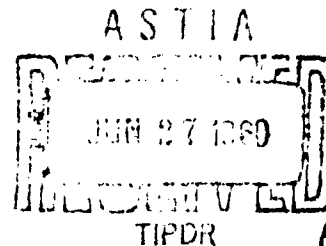
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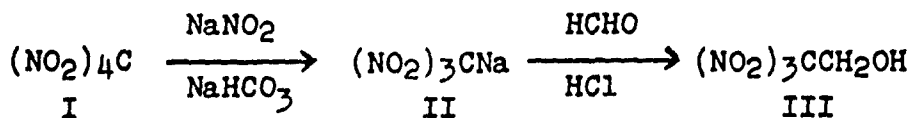
AN IMPROVED PROCESS FOR THE
PREPARATION OF 2,2,2-TRINITROETHANOL, TNEOH

Prepared by:

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ABSTRACT: An improved process for the preparation of 2,2,2-trinitroethanol, without isolation of intermediates, is described. Tetranitromethane, I, is reduced to sodium nitroform, II, which then is simultaneously acidified and formylated by a solution of paraformaldehyde in hydrochloric acid. The crude trinitroethanol, III, separates in 80-85% yield as an oil which can be stored safely. Pure crystalline trinitroethanol is obtained from chlorinated solvent solutions of the oil dried by azeotropic distillation.



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This report describes the development of an improved process of preparation of 2,2,2-trinitroethanol which was carried out under Task 301-664/43006/08, Explosives Applied Research. Because trinitroethanol is a primary intermediate, the work was undertaken in connection with the study of the synthesis of the oxygen-rich explosive compounds trinitroethyl orthocarbonate, TNEOC; bis(trinitroethyl) carbonate, BTNEC; and bis(trinitroethyl) formal, TEFO.

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Acting Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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AN IMPROVED PROCESS FOR THE
PREPARATION OF 2,2,2-TRINITROETHANOL, TNEOH

INTRODUCTION

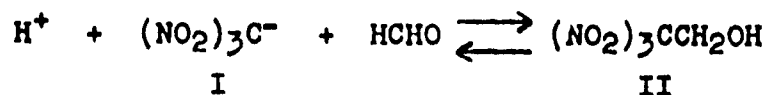
2,2,2-Trinitroethanol, TNEOH, has long been an important intermediate in the preparation of aliphatic polynitro compounds, since it affords one of the easiest means of introducing the trinitro group into an organic compound. The current interest in the oxygen rich explosive compounds, 2,2,2-trinitroethyl orthocarbonate, TNEOC, bis(2,2,2-trinitroethyl) carbonate, BTNEC, and bis(2,2,2-trinitroethyl) formal, TEFO, has focused attention on trinitroethanol since it is the basic intermediate in their preparation. The present study has been carried out in an attempt to improve the laboratory procedure for the preparation of trinitroethanol and also to collect information from scattered sources on its physical properties and characteristic reactions.

A review of the early history of nitroform and 2,2,2-trinitroethanol, with references, has been compiled by the Aerojet-General Corporation (1) and will only be supplemented and not be repeated here.

DISCUSSION AND RESULTS

Synthesis of 2,2,2-Trinitroethanol, TNEOH

A. Historical. The synthesis of 2,2,2-trinitroethanol, TNEOH, II, is according to the following equation:



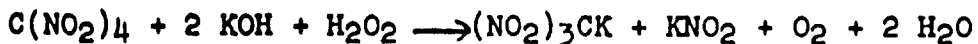
This is an equilibrium reaction, and the extent of formation of trinitroethanol is determined primarily by the pH of the reaction mixture. Above a pH 5.5 trinitroethanol largely exists in solution as its components, nitroform ion, I, and formaldehyde (2,23).

It is thus readily seen that the synthesis of trinitroethanol depends on the availability of nitroform.

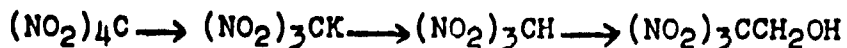
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Nitroform was first discovered in 1857 by Schischkoff (3) but it was in 1899 that it was prepared by Hantzsch and Rinckenberger (4) by the reduction of tetranitromethane, TNM, and since that time there has been extensive work on tetranitromethane and its reduction to nitroform (5). Tetranitromethane is a good oxidant and many common reducing agents have been used with it to produce nitroform, usually as the potassium salt. Hantzsch and Rinckenberger (4) used alcoholic potassium hydroxide, or "better potassium ethylate" to prepare potassium nitroform from tetranitromethane. However, somewhat later, Macbeth (6) warned against the use of sodium ethylate in this reaction because of his experience with an explosion in the laboratory. Macbeth and Orr (7) found glycerine a convenient reducing agent with potassium hydroxide, and glycerine was used in pilot plant production of potassium nitroform (8). Potassium sulfite, potassium ferrocyanide, arsenious acid, potassium phosphite, ammonium sulfide and hydrazine have all been used effectively to produce potassium nitroform from tetranitromethane (9).

One of the better methods previously used for the preparation of trinitroethanol from potassium nitroform is the process developed from Schimmelschmidt's work (10) by Aerojet-General Corporation (1), and later modified at the Naval Ordnance Laboratory (11). The potassium nitroform is prepared from tetranitromethane by reduction with hydrogen peroxide and potassium hydroxide according to the following equation:



The potassium nitroform can then be acidified and the resulting nitroform condensed with formaldehyde to produce trinitroethanol in high yield. The over-all series of reactions is:

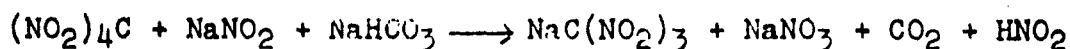


The reactions in the various steps proceed smoothly and the yields are good, the only difficulty arising from the necessity of handling the potassium nitroform. This intermediate has an impact sensitivity of 44 cm (tetryl = 40 cm) and is unstable in storage, even when stored under solvent (12). By using potassium nitroform the same day it is isolated the danger is

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minimized, but its use should be avoided if possible, and for large scale production of trinitroethanol would be very hazardous.

The use of potassium nitroform can be avoided by preparing the soluble sodium salt of nitroform by the Glover-Sickman reaction (13), which utilizes sodium nitrite and sodium bicarbonate for the reduction of tetranitromethane according to the following equation:



Dacons and Kamlet (14) studied this reaction rather extensively in preparing nitroform for the synthesis of 4,4,4-trinitrobutyric acid and established the conditions for good yields in the nitrite reduction of tetranitromethane. They then developed a "one-pot" synthesis of trinitroethanol (15) following the customary procedure of acidification of the alkali salt of nitroform and condensation of the free nitroform with 37% formalin solution to form trinitroethanol. They obtained dry trinitroethanol by adding methylene chloride to the reaction mixture and removing all of the water by azeotropic distillation.

The present authors have found that various simplifications of this method can be made, namely: the use of paraformaldehyde instead of formalin solution which obviates the necessity of analyzing the formalin and reduces the volume of water used; simultaneous acidification and formylation which shortens the reaction period appreciably; elimination of the heating period in the second step; and an improvement in the drying procedure for obtaining crystalline trinitroethanol or dry trinitroethanol in solution.

B. Optimum Procedure. For laboratory purposes, therefore, the sodium nitrite-sodium bicarbonate reduction of tetranitromethane appears to be the best procedure to follow in order to obtain nitroform for the synthesis of trinitroethanol. This reduction is carried out by adding tetranitromethane to a slurry of sodium nitrite and sodium bicarbonate in 50% methanol-water and holding at 55°-60°C for two and a half to three hours. During this period the color deepens from the original yellow to a reddish brown and the heterogeneous mixture becomes an homogeneous solution. The use of a slurry of the inorganic salts keeps the volume of the reaction medium within practical handling limits. Methanol is essential in the reaction medium

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to increase the solubility of the tetranitromethane since otherwise the extreme insolubility of tetranitromethane in water results in a very slow reaction rate. The tetranitromethane may be added to the slurry quite rapidly since there is no apparent exothermic or other detrimental reaction at this point. The reaction period of two and a half to three hours is necessary to insure complete reduction of the tetranitromethane.* The necessity of the long reaction period for the reduction of tetranitromethane to nitroform is verified not only by a lower yield realized from a shorter reaction period but by calculations based on a kinetic study of the reaction in aqueous medium by D. J. Glover (16).

The acidification of the basic reduction solution, and the formylation of the nitroform ion with formaldehyde is carried out in one step in the same container as was used for the reduction of tetranitromethane. Paraformaldehyde offers a convenient source of formaldehyde, easy to handle and readily depolymerized in concentrated hydrochloric acid. Such a solution is added rapidly to the tetranitromethane reduction solution after cooling the latter to room temperature. Some brown fumes of oxides of nitrogen are evolved, but there is no exothermic reaction beyond that expected from dilution of the acid. There is an abrupt color change from orange to lemon yellow when the solution becomes acid and a heavy lemon yellow oil separates immediately. The trinitroethanol formation is complete as soon as the acid-formaldehyde addition is complete and the oil can be separated from the aqueous layer immediately. Neither a prolonged reaction period nor a prolonged period at an elevated temperature produces an appreciable additional amount of product.

For laboratory purposes the aqueous layer can be discarded. It has been shown by extraction of the mother liquor with methylene chloride and isolation of crystalline trinitroethanol from the extract that the aqueous layer contains only about 5% of the total trinitroethanol obtained in the reaction, or 3.75% of the theoretical weight of trinitroethanol obtainable based on the amount of tetranitromethane used. On a larger than laboratory scale such extraction procedures would probably be justified.

* The preceding paragraph is essentially a repetition from Dacons and Kamlet (14) and is included here for clarity and completeness of discussion.

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Preparation of Dry Trinitroethanol. The oil layer contains principally trinitroethanol hydrate, with methanol, water, and some impurities including inorganic salts dissolved in the water present. Isolation of crystalline trinitroethanol from the oil is accomplished by dissolving the oil in a chlorinated solvent such as methylene chloride, chloroform, or carbon tetrachloride, drying the resulting solution by azeotropic distillation to concentrate the solution, and chilling the concentrated solution to cause crystallization.

Ordinary drying agents such as Drierite or magnesium sulfate are not adequate for isolating crystalline trinitroethanol. Either the trinitroethanol does not crystallize at all or the crystalline product is sticky and low melting. After drying the solution by azeotropic distillation, however, the trinitroethanol crystallizes in well formed crystals from which the solvent evaporates readily, leaving dry crystals. Carbon tetrachloride is probably the best solvent from which to crystallize trinitroethanol because it is easier to dry its solutions of trinitroethanol and also because pure trinitroethanol is only slightly soluble in carbon tetrachloride. However, the trinitroethanol oil is not very soluble in carbon tetrachloride and although the two phase system of oil-carbon tetrachloride can be dried by azeotropic distillation, such a system might be hazardous, especially in large quantity. Since the trinitroethanol oil is miscible with methylene chloride it was found preferable to dry the oil by azeotropic distillation of the methylene chloride-trinitroethanol oil solution, then add carbon tetrachloride and strip off the methylene chloride. Trinitroethanol crystallizes from the chilled carbon tetrachloride solution and is filtered off and dried. A yield of 80-85% of theoretical, based on the amount of tetranitromethane used is obtained by this isolation procedure. The product is a white crystalline material which melts at 74°C.

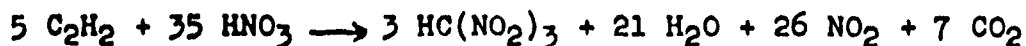
Dry crystalline trinitroethanol is a sensitive compound. Danger of handling can be decreased by keeping the trinitroethanol in solution after drying since, for many purposes, it is not necessary to isolate crystalline trinitroethanol. Trinitroethyl orthocarbonate, TNEOC, (17), bis(trinitroethyl) carbonate, BTNEC, (18), and bis(trinitroethyl) formal, TEFO, (19), preparations are carried out by using carbon tetrachloride solutions of trinitroethanol. The concentration of trinitroethanol in the carbon tetrachloride or other solvent used can be determined by spectrophotometric measurement.

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The method depends on alkaline extraction of the trinitroethanol from the solvent and the fact that in alkaline medium trinitroethanol is quantitatively decomposed to its components, nitroform and formaldehyde. Measurement of the absorbency at 350 mμ, characteristic of the nitroform ion, is used to determine the molar concentration of nitroform, and hence of trinitroethanol.

Other Methods of Preparation of Trinitroethanol. The above optimum process is adaptable to production on a large scale, but the long reaction period required in the reduction of tetranitromethane makes a continuous production method less feasible than desired. Other reducing agents, notably sodium sulfite and hydrazine, have been reported (9) as reducing tetranitromethane to nitroform rapidly and without detrimental side reactions. The work reported, however, involved the preparation of the insoluble potassium salt of nitroform and the use of alkaline solutions throughout, conditions which probably prevented secondary action of the reducing agent. These and other reducing agents were adapted to the "one-pot" synthesis as described above and it was found that the reaction time for the reduction of tetranitromethane could be shortened considerably. In fact the reduction was complete almost as fast as tetranitromethane was added to the reagent, but other considerations nullified the gain. Either serious side reactions, such as further reduction of the nitroform to the dinitro compound, or precipitation of side products as in the case of ferrous chloride, interfered in the reaction. In addition, the volume of solvent had to be increased so that in no case was the trinitroethanol obtained as an oil as it is in the sodium nitrite-sodium bicarbonate reduction method, and extensive extraction procedures were required to isolate crystalline trinitroethanol.

Large scale production of trinitroethanol, i.e. pilot plant or larger, will undoubtedly use nitroform produced by nitration of acetylene:



A feasibility study on an operation by this method at a rate of five tons per day was made at the Naval Ordnance Laboratory by Raymond W. Southworth (20). Production at the rate of one kilogram per hour has been in operation, and a plant designed to produce ten kilograms per hour is now being constructed (21).

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Wetterholm and Nilsson (22) patented a two step distillation process for obtaining an aqueous solution of nitroform from the reaction mixture in the acetylene nitration. First 98% nitric acid is distilled off under reduced pressure to minimize further nitration of the nitroform to tetranitromethane until the nitric acid-water ratio approaches that of the azeotropic mixture. Water is then added to the residue until the nitric acid concentration is reduced to about 60%. Distillation of this mixture (also under reduced pressure) gives an aqueous solution of nitroform containing 44.3% of nitroform, 55.2% of water and 0.5% of nitric acid. That trinitroethanol can be prepared from such a solution has been demonstrated by a brief study. A solution of pure nitroform and aqueous nitric acid of the composition given above was prepared and 37% formalin was added to the solution. A lemon yellow oil formed and by following the customary extraction and drying procedures a 77% yield of crystalline trinitroethanol was isolated from this reaction.

Physical Properties of Trinitroethanol. Pure trinitroethanol crystallizes from methylene chloride in massive transparent rods having a melting point of 73.5-74°C. The alcohol is stable in storage at room temperature either in crystalline form or as the crude oil. The crystalline material sublimes very slowly at atmospheric pressure and ambient temperatures of storage, depositing trinitroethanol elsewhere in the storage vessel over a period of time. Also on long standing the crystals have a tendency to cake but are easy to handle under normal laboratory conditions.

Various laboratories have reported that trinitroethanol is very hygroscopic. Experience has shown, however, that the pure crystals do not readily take up water. On days of relatively low humidity, typical of the winter months, recrystallized trinitroethanol can be "bench dried" successfully and handled without extreme precaution against atmospheric moisture. Crystals of the pure alcohol appear to sublime into the air, at least partially accompanied by a reversion to formaldehyde and nitroform which are easily detected in the space above the crystal surfaces. Even in a humid atmosphere, water take-up is rather slow if the compound is pure, but quite rapid if the recrystallized material contains impurities such as nitroform, formaldehyde, or water.

On occasion, pure trinitroethanol which had "oiled" by absorbing water was observed to crystallize again to crystals

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having a lower melting point. This observation, plus the ineffectiveness of common adsorbents for drying trinitroethanol oil solutions, indicated that the alcohol existed in the crude oil as the hydrate and that the low melting "pure trinitroethanol" reported by previous laboratories was really the crystalline monohydrate. Ostensibly the crude oil contained 20-30% water but all but a few per cent of the oil could be dissolved in carbon tetrachloride or methylene chloride, either of which could be an effective solvent for the monohydrate of trinitroethanol, but not for water. Further evidence on this point was obtained in one instance when it was observed that, after ordinary drying procedures were followed, azeotropic distillation removed the exact equivalent of one mole of water for the amount of crystalline trinitroethanol present in solution. It was then determined that well formed, but "soft" or "sticky" long needles can be obtained from dry crystalline trinitroethanol plus one mole of water. The trinitroethanol dissolved with endothermic heat of solution on addition of the water, but upon chilling or seeding the solution becomes a solid mass of beautiful long needles. Similar crystals can be obtained by evaporation of the residual mother liquor from the trinitroethanol oil, or from a methylene chloride solution of the oil. The melting point of the crystals from the three sources was the same, 60-62°C. However, crystals of the hydrate as obtained above were allowed to stand in the open overnight in an atmosphere of low humidity and the next day the melting point was 52°C and quite sharp at that point. This observation seems to indicate that the crystalline hydrate may vary in water content. It is also assumed that the fact that trinitroethanol forms hydrated crystals probably accounts for the different melting points, 30°C to 74°C, reported for "pure trinitroethanol" by various authors. Table I summarizes the general physical properties of trinitroethanol.

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TABLE I

Physical Properties of Trinitroethanol

Melting Point	73.5-74°C
Crystal Density	1.70
Impact Sensitivity (50% Height, 2.5 kg weight)	11 cm (pure crystals RDX=24 cm) 25 cm (wet with CCl ₄) 22 cm (monohydrate) 86-101 cm (as crude production oil)
Vacuum Stability	Sublimes easily under reduced pressure
Solubility (room temperature)	Soluble in water, chloroform, methanol, methylene chloride Very soluble in glacial acetic acid Slightly soluble in hexane, carbon tetrachloride (v.s. hot)
Equilibrium Constant	1.4×10^{-5} (TNEOH $\xrightarrow{H_2O}$ HCHO + HC(NO ₂) ₃) (ref. 23)

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Chemical Reactions of Trinitroethanol. Trinitroethanol derivatives have been among the most important compounds evaluated during the new explosives program. Nitro groups constitute 76% of the trinitroethanol molecule and for aluminized compositions trinitroethanol is one of the most efficient intermediates for introducing oxygen into an explosive compound.

Although trinitroethanol has the structure of an alcohol, the polar effect of the nitro groups decreases the reactivity of the hydroxyl group to a very great degree. Esterifications, acetal formation and other reactions which involve the basic properties of the hydroxyl group are difficult to carry out under normal conditions. Processes which proceed through a carbonium ion intermediate are unknown. Ether formation via the alkoxide or any reaction requiring basic conditions cannot be realized because of the dissociation of the alcohol at higher pH's. For reactions which occur under acidic conditions several unusual methods are being used to circumvent the unreactivity of trinitroethanol.

Some of the most recently studied reactions of trinitroethanol are discussed briefly below and others are outlined in Table II.

1. Esterification. The very weak basicity of the hydroxyl group of trinitroethanol was quite evident when attempts were made to esterify the alcohol with aliphatic or aromatic acids by the usual classical methods. Even with acid chlorides long reaction periods were required in most cases to obtain low yield of ester. Since organic esters are an important class of compounds for evaluation as explosives, several processes were devised which greatly speeded up the esterification of trinitroethanol. An unusual method of direct esterification, most useful for the preparation of trinitroethyl trinitrobutyrate, TNETB, consisted of employing 100% sulfuric acid as solvent (24). The product precipitated from the sulfuric acid and was easily isolated in high yield. Fuming sulfuric acid was used for the transesterification of methyl trinitrobutyrate (25) with trinitroethanol as an alternative process. The sulfuric acid method was limited to the reaction of trinitroethanol with strong organic acids in order to get a favorable equilibrium between the formation of the product and the opposing cleavage reaction. A more general procedure for the preparation of trinitroethanol esters consisted of the reaction of acid chlorides with the alcohol in the presence of catalytic amounts of metal halides. High

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yields were obtained at reaction rates several hundredfold faster than previously realized (26). Trifluoroacetic anhydride (27) was also used successfully as a solvent for direct esterification.

2. Acetal Formation. The formation of acetals of trinitroethanol by the usual methods has not been particularly successful. Recently, however, high yields of formals have been obtained by the reaction of trinitroethanol and some other nitro alcohols with paraformaldehyde using strong sulfuric acid as solvent at room temperature (19). The product, bis(trinitroethyl) formal, precipitated from the sulfuric acid solution.

3. Orthoester Formation. A new reaction of poly-halogen compounds, $RCCl_3$, with trinitroethanol in the presence of ferric chloride has provided a family of orthoesters of trinitroethanol which are unusually high in oxygen content. One of these, trinitroethyl orthocarbonate, $(TNEO)_4C$, was obtained in high yield from carbon tetrachloride, trinitroethanol and ferric chloride under strictly anhydrous conditions (17). In a modification of this reaction, the system was kept moist by the addition of water in order to obtain trinitroethyl chlorocarbonate by hydrolysis of the partially substituted carbon tetrachloride intermediate. The chlorocarbonate was then converted to bis(trinitroethyl) carbonate by reaction with trinitroethanol in a separate step using metal halide catalysis (18).

4. Urethane Formation. After lack of success early in the program in preparing trinitroethyl urethanes from isocyanates, ferric acetyl acetate was found to be a good catalyst for the reaction of trinitroethanol with various isocyanates (28).

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TABLE II
Reactions of Trinitroethanol

<u>TNEOH Reaction with:</u>	<u>Conditions</u>	<u>Product</u>	
1. Acids	a) 100% H ₂ SO ₄ , 50°C b) (CF ₃ CO) ₂ O	TNE esters TNE esters	(24) (27)
2. Esters	Fuming H ₂ SO ₄	TNE esters	(25)
3. Acid chlorides	AlCl ₃ catalyst	TNE esters	(28)
4. Formaldehyde	Concentrated H ₂ SO ₄ , 25°C	Bis(TNE) formal	(19)
5. RCOCl compounds	a) Anhydrous FeCl ₃ b) H ₂ O-FeCl ₃ -RCOCl	a) TNE orthoesters b) TNEOCR	(17) (17)
6. Ammonia	H ₂ O solution	Bis(TNE) amine	(29)
7. Isocyanates	Ferric acetyl acetate catalyst	TNE Urethanes	(28)
8. RNHC(=O)Cl	Fusion	TNE Urethanes	(29)
9. (RNH) ₂ C=O	MeOH	TNE substituted Ureas	(29)
10. RSO ₂ NH ₂	Fusion	TNE sulfonamides	(29)
11. HNO ₃	H ₂ SO ₄	TNEONO ₂	(29)
12. PCl ₅	HCl catalyst	TNE chloride and TNE phosphate	(30)
13. SOCl ₂	CCl ₄	(TNEO) ₂ SO	(31)
14. AlCl ₃	CCl ₄	TNEOH Cl ₂	(26)

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ACKNOWLEDGMENT

The authors gratefully acknowledge their indebtedness to other members of the Organic Chemistry Division for their assistance in this project:

To Dr. J. C. Dacons for discussion of the sodium nitrite reduction of tetranitromethane; to Mr. D. J. Glover for assistance in making the spectrophotometric measurements and interpreting the results of those measurements; to Mr. H. T. Simmons for crystal density determination.

The impact sensitivities were determined by Mrs. Sarah Duck of the Chemical Engineering Division of the Chemistry Research Department.

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EXPERIMENTAL

Synthesis of Trinitroethanol Oil

A. By sodium nitrite-sodium bicarbonate reduction of tetranitromethane (optimum procedure). A slurry of 78 g (1.15 mole) of sodium nitrite and 95 g (1.15 mole) of sodium bicarbonate (Note 1), 190 ml of methanol and 190 ml of distilled water was heated to 55°C in a 2 liter, 3-neck, round bottom flask fitted with a thermometer, mechanical stirrer and a Claisen adapter with a Friedrich condenser and dropping funnel. With vigorous stirring, 125 ml (1.0 mole) of tetranitromethane was added over a period of 10 minutes (Note 2). The temperature was maintained at 55-60°C for two and a half to three hours after the addition of the tetranitromethane was completed (Note 3). The reaction mixture was then cooled to room temperature and a solution of 36 g (1.2 mole) of paraformaldehyde dissolved in 125 ml (1.25 mole) of concentrated hydrochloric acid was added fairly rapidly (Note 4). The mixture was stirred for 15 minutes to insure complete reaction and then transferred to a separatory funnel and the trinitroethanol oil was separated from the supernatant aqueous layer (Note 5). The oil weighed 250 g. It can be stored safely or used for the preparation of dry crystalline trinitroethanol.

Note 1. Greater quantities of sodium bicarbonate, 1.5 moles and 2.0 moles, were used in different preparations. The yield of crystalline trinitroethanol was not changed appreciably by using a larger quantity of sodium bicarbonate and handling difficulties were increased.

Note 2. The mixture became yellow immediately upon addition of tetranitromethane.

Note 3. During the heating period the color deepened from yellow to reddish orange. The inorganic salts dissolved completely after about 45 minutes and the solution became completely homogeneous, i.e. no visible droplets of tetranitromethane, before the end of the reaction period.

Note 4. Brown fumes of oxides of nitrogen were always evolved during the first part of this addition, but no exotherm beyond that expected by dilution of the concentrated hydrochloric acid was noted, or other indication of detrimental reaction. The color of the solution lightened from reddish

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orange to orange during the addition of the acid-formaldehyde mixture and there was an abrupt change from orange to lemon yellow when the solution became sufficiently acid, accompanied by the formation of droplets of a lemon yellow oil.

Note 5. The aqueous layer has been shown to contain only about 5% of the trinitroethanol produced in the reaction and may be discarded or, if so desired, the trinitroethanol may be extracted with methylene chloride.

B. By sodium sulfite reduction of tetranitromethane. A slurry of 19.0 g (0.075 mole) of sodium sulfite ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$), 8.4 g (0.10 mole) of sodium bicarbonate, 50 ml methanol and 50 ml of distilled water was heated to 50°C in a 500 ml, 3-neck, round bottom flask fitted with a thermometer, mechanical stirrer and a Claisen adapter with a Friedrich condenser and a dropping funnel. External heating was discontinued during the addition of 6 ml (0.05 mole) of tetranitromethane, the temperature being maintained during the ten minutes of addition by the exotherm of the reaction. Heating was then resumed and continued for one hour. After cooling to room temperature the solution was acidified by the addition of 20 ml of concentrated hydrochloric acid containing 1.75 g (0.05 mole) of paraformaldehyde. The resulting lemon yellow solution was filtered from a small amount of inorganic salt and extracted with five 25 ml portions of methylene chloride. The methylene chloride solution was dried by azeotropic distillation with a reverse Dean-Stark trap and the methylene chloride was removed by evacuation in vacuo. The residue was dissolved in 20 ml of carbon tetrachloride and the solution was chilled. The crystalline product which formed weighed 6.1 g or 67.4% of theoretical yield, m.p. $73.5\text{--}74^\circ\text{C}$.

The reduction of tetranitromethane was followed by spectrophotometric measurements on samples withdrawn from the reaction mixture 5 minutes, 8 minutes and 15 minutes after the addition of tetranitromethane was completed. These analyses indicated that reduction of the tetranitromethane was complete within a few minutes.

However, it was found that, whereas the maximum absorbency for nitroform should be at 350 $\text{m}\mu$, in these solutions the maximum was shifted toward 360 $\text{m}\mu$, the peak for

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dinitromethane. By calculating from known constants for nitroform and dinitromethane it was estimated that 6.6% of the total reduction product of TNM in the mixture was dinitromethane rather than nitroform.

C. By hydrazine reduction of tetranitromethane. The preparation was carried out as with sodium sulfite-sodium bicarbonate only using hydrazine sulfate and sodium bicarbonate at room temperature. In alkaline solution hydrazine is known to reduce tetranitromethane only as far as nitroform (9). Acidification as in the second stage of the TNEOH synthesis, however, produced a solution of intense orange color instead of the usual lemon yellow. Spectrophotometric measurements showed a shift in the maximum absorbency from 350 mu, maximum for nitroform, toward 360 mu, maximum for dinitromethane. By calculations based on known constants for nitroform and dinitromethane it was estimated that 20% of the reduction product formed in this reaction was the dinitro compound.

D. By hydrogen peroxide and sodium hydroxide reduction of tetranitromethane. The formation of the sodium salt of nitroform was carried out with sodium hydroxide and hydrogen peroxide, duplicating the procedure for potassium nitroform (11). Acidification and formylation as in the synthesis from the sodium nitrite-sodium bicarbonate reduction above produced no oil, but a 50% yield of crystalline trinitroethanol was isolated from the reaction solution by extraction with methylene chloride.

E. Ferrous chloride reduction of tetranitromethane. A small scale, test tube, experiment using ferrous chloride and sodium bicarbonate for the reduction of tetranitromethane showed that ~~tetranitromethane~~ tetranitromethane was indeed reduced by ferrous chloride in alkaline solution as determined by spectrophotometric measurement of the nitroform in the solution. When the preparation was scaled up to 0.05 mole, however, the ferric hydroxide present in the alkaline mixture formed a thick gel which presented such difficulty in filtering that the method was considered impractical and not developed further.

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Isolation of Crystalline Trinitroethanol

A. By drying a methylene chloride extract.

1. From the crude trinitroethanol oil layer. The oil layer from a 1.0 mole preparation of trinitroethanol, 252.7 g, was dissolved in 350 ml of methylene chloride. The solution was dried by refluxing for 5-6 hours with a reverse Dean-Stark trap. The dry solution was decanted from the inorganic salts which separated from the solution during drying, and chilled. The crystalline product which formed was filtered off and dried. It weighed 107.5 g. The filtrate was reduced to half volume by evaporation in vacuo, then chilled, and the second crop of crystals was filtered off and dried. This weight was 33.6 g. The combined yield from the oil layer was 141.1 g, or 78% of theoretical, m.p. 73-74° C.

2. From the aqueous mother liquor. The aqueous mother liquor from the same 1.0 mole preparation of trinitroethanol as in 1, above, was extracted with five 25 ml portions of methylene chloride. The combined methylene chloride solutions were dried by azeotropic distillation, the volume of the solution was reduced to about 25 ml by evaporation in vacuo, and the solution was chilled. The crystalline product which formed was filtered off and dried. It weighed 6.8 g, 3.75% of theoretical, or 4.6% of the total weight of trinitroethanol isolated from the reaction, m.p. 73-74°C. The combined yield from oil and aqueous layers as crystalline trinitroethanol was 147.9 g or 83% of the theoretical.

B. By drying a carbon tetrachloride solution. A portion, 50 g, 20% of the oil obtained from a 1.0 mole preparation of trinitroethanol, of trinitroethanol oil was added to 150 ml of carbon tetrachloride in a 300 ml round bottom flask and the mixture was refluxed with a reverse Dean-Stark trap to remove the water present. The dry carbon tetrachloride solution was decanted from the inorganic salts which separated during the azeotropic distillation and chilled. The crystalline product which formed was filtered off and dried. It weighed 29.1 g, m.p. 73.5-74°C. The total yield of trinitroethanol on this basis would be 145.5 g, or 80.5% of the theoretical in the oil layer. Assuming

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7.0 g in the aqueous layer as determined in A-2 above, the total yield of crystalline trinitroethanol would be 152.5 g, or 84.3% of theoretical.

C. By drying a methylene chloride-carbon tetrachloride solution. The mother liquor from a 1.0 mole preparation of trinitroethanol was extracted with six 50 ml portions of methylene chloride. This extract was added to the trinitroethanol oil, 247.3 g, formed in the preparation, to form 460 ml of solution. A portion of this solution, 100 ml, was added to 100 ml of carbon tetrachloride and the mixture was dried by azeotropic distillation with a reverse Dean-Stark trap for three hours. The dry solution was decanted from the inorganic salts which separated during the drying, the methylene chloride was stripped from the solution by distillation, the carbon tetrachloride solution was chilled and the white crystalline product which formed was filtered off and dried. It weighed 33.9 g, m.p. 73.5-74°C. The total weight of trinitroethanol on this basis would be 155.9 g, or 86% of the theoretical based on the weight of tetranitromethane used in the trinitroethanol preparation.

Preparation of Trinitroethanol Hydrate. Water, 0.5 g (0.0275 mole) was added to 5 g (0.0275 mole) of dry crystalline trinitroethanol in a 25 ml erlenmeyer flask. The trinitroethanol dissolved with endothermic heat of solution. Chilling the solution produced a solid mass of crystalline material, or a small amount of the solution on a watch glass crystallized to a solid mass of long needles when seeded with a crystal of the chilled product.

A small amount of trinitroethanol oil was allowed to stand in the open at room temperature in an atmosphere of low humidity. Long needle like crystals, similar in shape to those from dry crystalline trinitroethanol plus water formed. Similar crystals were also obtained by allowing a small amount of a methylene chloride solution of crude trinitroethanol oil to stand on a watch glass at room temperature in an atmosphere of low humidity.

Crystals from the three sources, crystalline trinitroethanol plus water, trinitroethanol oil, and a methylene chloride solution of trinitroethanol oil, melted at the same temperature on a hot stage, 60-62°C. After standing over night in an atmosphere of low humidity, however, the crystals melted sharply at 52°C.

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